GROWTH OF COMPOUND SEMICONDUCTORS IN A LOW GRAVITY ENVIRONMENT: MICROGRAVITY GROWTH OF PbSnTe

S40-27

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The growth of the alloy compound semiconductor lead tin telluride (PbSnTe) was chosen for a microgravity flight experiment in the Advanced Automated Directional Solidification Furnace (AADSF), on the United States Microgravity Payload-3 (USMP-3) and on USMP-4 Space Shuttle flights in February, 1996, and November, 1997.

The objective of these experiments was to determine the effect of the reduction in convection, during the growth process, brought about by the microgravity environment. The properties of devices made from PbSnTe are dependent on the ratio of the elemental components in the starting crystal. Compositional uniformity in the crystal is only obtained if there is no significant mixing in the liquid during growth. Lead tin telluride is an alloy of PbTe and SnTe. The technological importance of PbSnTe lies in its band gap versus composition diagram which has a zero energy crossing at approximately 40% SnTe. This facilitates the construction of long wavelength (>6 μm) infrared detectors and lasers. The properties and utilization of PbSnTe are the subject of other papers.[1,2]

PbSnTe is also interesting from a purely scientific point of view. It is, potentially, both solutally and thermally unstable due to the temperature and density gradients present during growth. Density gradients, through thermal expansion, are imposed in directional solidification because temperature gradients are required to extract heat. Solutal gradients occur in directional solidification of alloys due to segregation at the interface. Usually the gradients vary with both experiment design and inherent materials properties.

In a simplified one dimensional analysis with the growth axis parallel to the gravity vector, only one of the two instabilities work at a time. During growth, the temperature in the liquid increases ahead of the interface. Therefore the density, due to thermal expansion, is decreasing in that direction. However, the phase diagram shows that the lighter SnTe is preferentially rejected at the interface. This causes the liquid density to increase with distance away from the interface.

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The PbSnTe growth experiment on USMP-3 consisted of three separate crystals grown in a single segmented ampoule. The crystals were grown in series, one in each of the three primary orientations with respect to the residual gravity vector. The growths on USMP-3 were roughly analogous to hot-on-top, cold-on-top, and horizontal growth.

The work on USMP-4 was to grow two sets of three crystals, again in segmented ampoules. The hot on top orientation was chosen for all growths. The variables, this time, were to be ampoule translation rate, thermal gradient, internal pressure, and nucleation procedure. The growth rate, which is related to the translation rate, is a key growth parameter under control of the experimenter. Higher growth rates produce steeper solutal gradients but less penetration of this vital diffusion zone into the convecting fluid flow. Thus, the growth rate presents a dichotomy of effects; a high growth rate produces a steeper concentration gradient while a low growth rate allows the diffusion tail to extend into the thermal convection cells. A change in thermal gradient has the obvious effect of changing the temperature dilatation contribution to the convective driving force. The internal pressure, at elevated temperatures, was adjusted by the amount of excess tellurium in the compound, and it was thought that it may affect pore formation in the crystals. The nucleation procedure was studied by using both seeded and unseeded growths and tests the influence of the evolution of latent heat on initial growth.

For the combined two flights we designed a set of nine experiments in three different ampoules to measure the effect of the gravitational body force on the convective properties of alloy compound crystal growth as modified by reduced gravity and other crystal growth parameters. As is often the case, especially in new and difficult experimental arenas such as found using the microgravity laboratory, nature may have her way with even the best laid plans of human endeavor and can wreck total havoc with strategies such as ours.

Ampoule #1 processed without any problems that were telemetered to the ground. Recalescence was observed in cells 1 and 2, and due to failure of the uppermost thermocouples (not a surprising event due the operating limits of the 20 mil diameter sheaths) was not expected to be observed in cell 3.

The observations, as seen on the ground, for our second ampoule (the third ampoule on the USMP-4 flight) were not so gratifying. On this part of the experiment, anomalies were observed in the sample thermocouples during the initial melting of the samples. When control thermocouples failed on the furnace booster heater, a cell (ampoule) failure and leakage from one of the lead tin telluride samples was suspected. To protect the two experiments already processed, the furnace drive was sent to the store position (full insertion), and growth was started in a gradient freeze manner by selectively powering down the different furnace zones. The experiment was terminated when the main heater control thermocouples failed.

The actual anomalies were only identified during sample retrieval at the Kennedy Space Center in February 1998. Clearly, the anomaly first occurred in ampoule # 1 not our second ampoule as was suspected. Cell 1, of ampoule #1, was intact and cell 2 was broken with approximately one third the length of the crystal still in the broken ampoule. The Inconel cartridge was swollen along its length starting near the cold end of cell 1, which was heated to 1000 C; the swelling

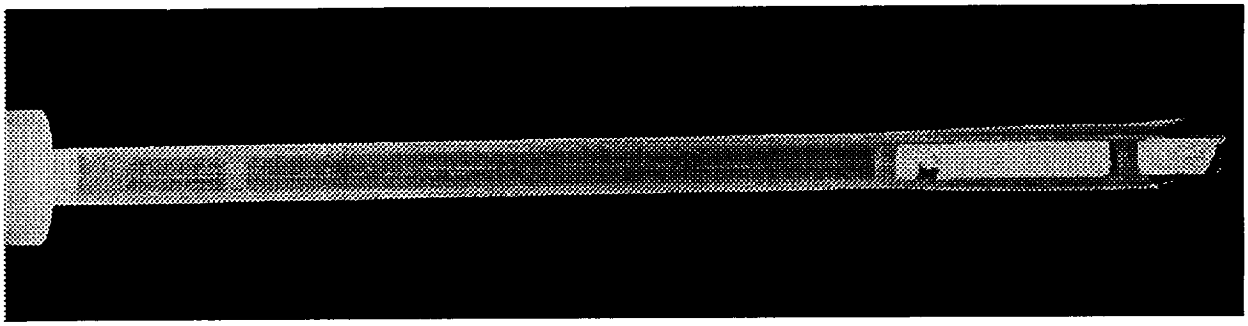

Figure 1. X-ray of sample AF-1 showing intact cell1, broken crystal in cell 2, and the swollen and torn Inconel cartridge.

increased at the beginning of cell 2, where the temperature had increased to 1150 C; and then the cartridge appeared ripped apart in the vicinity of the ampoule breakage. The remainder of the cartridge and ampoule were deposited in the furnace and caused the observed problems during the space processing of ampoule #2.

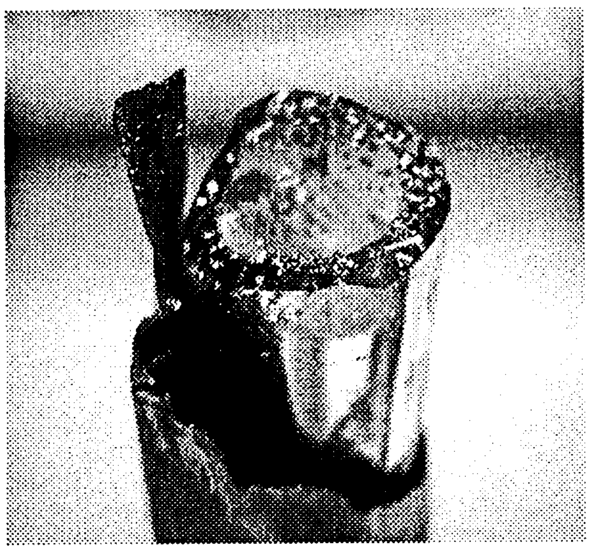

Figure 2. Photograph on the broken crystal and torn cartridge of AF-1.

The experimental ampoules, that is, what is left of them, are still impounded by the Marshall Space Flight Center awaiting further analysis of the anomaly; hence sample analysis must await their release. The remainder of this paper will discuss the observations made to date and attempts to duplicate the cartridge swelling that apparently caused the anomaly.

Figure 1 is an x-ray of the ruptured sample showing the completed cell 1 and the broken sample in cell 2 along with swelling of the cartridge. Figure 2 is a photograph of the broken end on cell 2. The metal cartridge appears forcibly torn and not corroded by PbSnTe vapors, and the remaining crystal in cell 2 appears to be broken and not just decanted from spilled liquid.

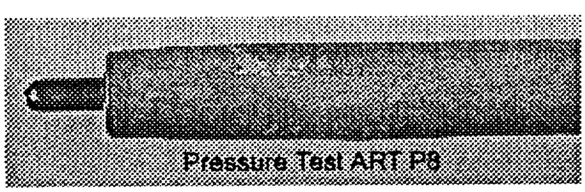

Figure 3. Result of pressure test where cartridge was pressurized to 75 psig.

A set of experiments was conducted at the Langley Research Center to determine if excess pressure within the cartridge (that is, the space between the sealed quartz ampoule and the Inconel cartridge) could have caused the cartridge to swell to a diameter greater than the 0.75 inch diameter of the radiation shield insert in the insulation zone of the furnace. The maximum excess pressure within the cartridge during growth in the AADSF is approximately 10 psi if the cartridges are sealed at 12 psia. In these post- flight tests the argon pressure was actively controlled at pressures up to 100 psig to simulate the remote possibility that the flight sample was over pressurized during sample preparation. Table 1 summarizes these tests and figure 3 shows one of the tubes after failure where the maximum bulge reached 0.70 inches only in the area of the failure. Three separate Inconel tubes were taken to failure (that is, an observation of pressure drop in the cartridge), but none produced sufficient swelling to have caught on the radiation shield and caused the tearing of the cartridge as observed on the flight sample.

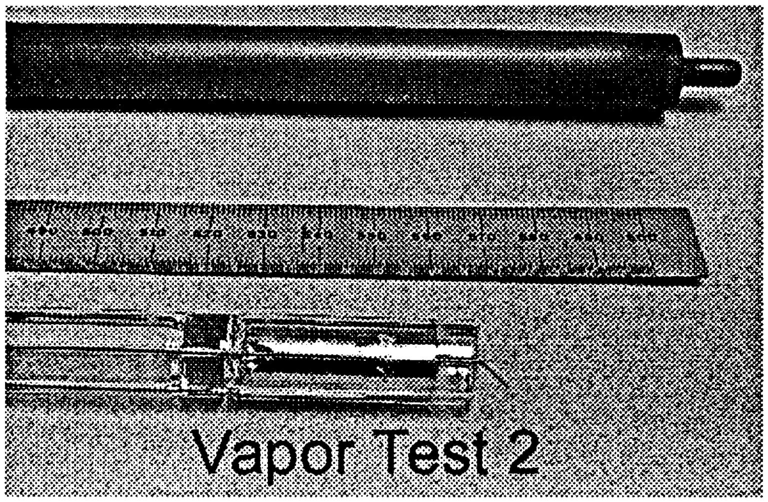

Figure 4. Setup for a PbSnTe vapor test on the integrity of the Inconel cartridge. The PbSnTe resides in the open ended quartz ampoule.

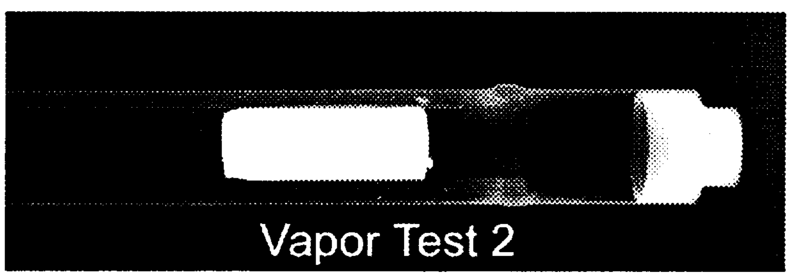

Figure 5. X-ray of loaded test cartridge after failure. Note that the only appreciable swelling (~0.66 inch) is immediately ahead of the open end of the ampoule.

Another set of tests looked at the hypothesis that one of the cells developed a crack and leaking PbSnTe vapor weakened the Inconel to allow the concomitant swelling. (Note: had the quartz containing the PbSnTe broken and liquid come in contact with the Inconel then the metal would have lost its integrity within seconds relieving any pressure differential.) As a cracked ampoule is difficult to simulate, we used an open ended ampoule that was maintained vertical to prevent any PbSnTe - Inconel contact. Figure 4 shows the open ended ampoule with the PbSnTe and the Inconel muffle tube which will contain it, and figure 5 is an x-ray of the sample after the failure as demonstrated by a pressure drop. Note that the only appreciable swelling occurred at the end of the open ampoule but even that was insufficient to bind on the AADSF insert.

The ampoules and furnace reside at the Marshall Space Flight Center awaiting deposition by the Anomaly Resolution Team. The two ampoules, still in their cartridges, have only been examined by computer aided tomography, x-rays, and photography. Further results must wait for the release of the samples and the subsequent analysis.

REFERENCES:

1. T.C. Harman; "Control and Imperfections in Crystals of PbSnTe, PbSnSe and PbSSe"; J.Nonmetals 1 (1973) 183.

2. S.G. Parker and R.W. Johnson; "Preparation and Properties of PbSnTe"; in Preparation and Properties of Solid State Materials vol 6, Ed. W.R. Wilcox, Marcel Dekker, Inc., New York 1981, p 1.

Table 1: Effect of Pressure, Temperature, and Time on Muffle Tube Expansion

This series of experiments examine the combined effect of temperature, pressure and duration on the expansion of the Inconel muffle tubes. All tubes used were from the same batch as the flight (AF1-105) tube, and the tests were conducted in the Bridgman furnace at Langley. ART-P1 through P6 involved heating the muffle tubes during the day, cooling overnight, and measuring the tube diameter, before proceeding to the next heat/cool/measure cycle. ART-P9 is a variation of the P7 and P8 tests, but without cooling and measuring the tube diameter after the 24 hours at 1000 C and 75 psig.

Number	Dates	psig	Temp °C	Time hr	Post-Test Tube Dia,	(increase) inches	Notes
ART-P1	3/18/98	15	1000	7:00	0.624	(0.000)	Muffle Tube # N25
ART-P2	3/19/98	15	1150	6:30	0.627	(0.003)	Followed ART-P1, same tube (N25)
ART-P3	3/20/98	25	1150	6:20	0.629	(0.002)	Followed ART-P2, same tube (N25)
ART-P4	3/23/98	45	1150	6:46	0.638	(0.009)	Followed ART-P3, same tube (N25)
ART-P5	3/24/98	75	1150	6:53	0.665	(0.027)	Followed ART-P4, same tube (N25)
ART-P6	3/25/98	100	1150	0:44	0.687	(0.022)	Leak developed in N25, test terminated.
ART-P7	4/2/98	75	1000	24:00	0.645	(0.021)	Muffle Tube # N27
ART-P8	4/6/98	75	1150	0:36	0.685 0.700 at split	(0.040)	Leak developed in N27, test terminated. Tube split 2" from tip.
ART-P9	4/8/98	75	1000	24:00	Not measured		Muffle Tube # N28 Straight to 1150C
ART-P9#2	4/9/98	75	1150	0:47	0.674	(0.050)	Leak developed in N28, test terminated.